Part B, Volume 1, No. 8, August 1963

Journal of Polymer Science, Part B

Polymer Letters

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POLYMER LETTERS VOL. 1, PP. 405-408 (1963)

MOLECULAR STRUCTURES OF THE DI-ISOTACTIC POLYMERS PREPARED FROM TRANS- AND CIS-1-DEUTEROPROPYLENES*

Natta and his co-workers (1,2) have reported that the di-isotactic polymers obtained from trans- and cis-1-deuteropropylenes by anionic type polymerization show the similar x-ray diagrams, but give the infrared spectra remarkably different from one another. From the evidence they have suggested two types of structures indicated with the prefixes "threo" and "erythro." However, it has remained as an unsettled problem which type of these two polymers is obtained from either of the monomers. In this communication we wish to report the results of the attempted determination of the molecular structures of these polymers by

TABLE I

Molecular Vibrations of IPP (A Species)[a]

Frequency, $cm.^{-1}$			Assignment
Obs.		Calcd.	
1456	vs	1456	$\delta(CH_3)$
1450	vs	1457	$\delta(CH_3)$
1435	m	1438	$\delta(CH_2)$
1376	vs	1352	$\delta_s(CH_3)$
1357	s	1397	$\delta(CH)$
1326	vw	1344	$w(CH)$, $\nu(CC)$
1305	w	1293	$w(CH_2)$, $\delta(CH)$
1255	w	1269	$t(CH_2)$
1166	m	1125	$\nu(CC)$, $r(CH_3)$, $w(CH)$
1043	vw	1058	$\nu(CC)$
998	m	1021	$r(CH_3)$
974	m	935	$r(CH_3)$, $\nu(CC)$
900	vw	874	$\nu(CC)$, $r(CH_3)$
841	m	826	$r(CH_2)$
452	w	451	$w(C-CH_3)$
396	vw	375	$\delta(CC)$, $\delta(C-CH_3)$
248	vw	248	$\delta(CC)$, $w(C-CH_3)$, $\delta(C-CH_3)$
–		109	$\delta(CC)$, $\delta(C-CH_3)$

[a]Maximum deviation: 5.60%, average deviation: 1.79%.

*This paper was read at the 16th Annual Meeting of the Chemical Society of Japan in Tokyo, March 31, 1963. The similar conclusion was also reported independently by T. Miyazawa et al. at the same Meeting.

TABLE II

Molecular Vibrations of DIPDP's (A Species). Poly-trans-1-Deuteropropylene (Obs.) (2) and Threo DIPDP (Calcd.)[a]

Frequency, cm.$^{-1}$			Assignment
Obs.		Calcd.	
1461	vs	1456	$\delta(CH_3)$
1452	vs	1457	$\delta(CH_3)$
1379	m	1397	$\delta(CH)$
1376	vs	1352	$\delta_s(CH_3)$
1328	m	1344	w(CH), ν(CC)
1281	m	1288	w(CHD), t(CHD)
1252	m	1276	δ(CHD)
1180	m	1145	ν(CC)
1075	m	1066	ν(CC), r(CH_3)
1038	m	1028	ν(CC), r(CH_3)
993	s	972	r(CH_3), t(CHD)
894	w	890	r(CH_3), ν(CC)
816	m	864	ν(CC)
719	m	717	r(CHD)
–		433	w(C–CH_3)
–		362	δ(CC), δ(C–CH_3)
–		244	δ(CC), w(C–CH_3), δ(C–CH_3)
–		104	δ(CC), δ(C–CH_3)

[a]Maximum deviation: 5.88%, average deviation: 1.49%.

comparing the infrared spectra of the polymers obtained from the two isomeric monomers (Peraldo and Farina (2)), with the results of the normal coordinate treatment made for the threo- and erythro-models.

The calculations were made by the GF matrix method with the Urey-Bradley force field, and the factoring of the matrices was made according to the method reported previously (3). The force constants were at first transferred from aliphatic hydrocarbons (4), and then modified to explain the observed data for isotactic polypropylene (IPP), poly-a,β, β-trideuteropropylene $(-CD_2C(CH_3)D-)_n$, and polyhexadeuteropropylene $(-CD_2C(CD_3)D-)_n$. (The latter two deuteropolymers were synthesized in this laboratory (5). The values of force constants used are as follows: K(CC) = 2.47 md/A, H(CCC) = 0.35, H(CCH)(CH_3) = 0.221, H(CCH)(CH_2) = 0.240, H(CCH)(CH) = 0.249, H(HCH)(CH_3) = 0.407, H(HCH)(CH_2) = 0.387, H(HCC)(CH) = 0.309, F(HH)(CH_3) = 0.100, F(HH)(CH_2) = 0.121, F(CH)(CH_3) = F(CH)(CH_2) = 0.433, F(CH)(CH) = 0.400, F(CC) = 0.200, $\kappa(CH_3)$ = –0.030 md·A, $\kappa(CH_2)$ = –0.020, κ(CH) = 0.030, and F′ = – 0.1 F. The results for IPP (the A species) are given

TABLE III

Molecular Vibrations of DIPDP's (A Species). Poly-cis-1-Deuteropropylene (Obs.) (2) and Erythro DIPDP (Calcd.)[a]

Frequency, $cm.^{-1}$			Assignment
Obs.		Calcd.	
1462	vs	1456	$\delta(CH_3)$
1452	vs	1457	$\delta(CH_3)$
1377	vs	1350	$\delta_s(CH_3)$
1361	m	1391	δ(CH)
1319	vvw	1342	w(CH)
1286	m	1288	δ(CHD), w(CHD)
1273	m	1274	δ(CHD), w(CHD), t(CHD)
1174	m	1151	ν(CC), t(CHD)
1121	m	1088	$r(CH_3)$, ν(CC)
1033	m	1045	ν(CC)
975	m	960	$r(CH_3)$
873	s	904	$r(CH_3)$
850	sh	804	t(CHD), ν(CC)
746	m	734	r(CHD)
–		444	$w(C-CH_3)$
–		367	δ(CC), $\delta(C-CH_3)$
–		234	δ(CC), $w(C-CH_3)$, $\delta(C-CH_3)$,
–		106	δ(CC), $\delta(C-CH_3)$

[a]Maximum deviation: 5.41%, average deviation: 1.79%.

in Table I, which shows good agreement between the observed and calculated frequencies. The maximum and average deviations are also given.

In Tables II and III the frequencies calculated by use of the same force constants for the threo- and erythro-models of the di-isotactic poly-1-deuteropropylenes (DIPDP's) are compared with the observed data (2) for the two polymers obtained from trans- and cis-1-deuteropropylenes, respectively. The dichroism, frequency and intensity of the bands of these two polymers, can be interpreted fairly well by the results of the present calculations in the case of this correspondence. Such a correspondence seems to be far more reasonable than the reverse one. From this result we may infer that the threo- and erythro-DIPDP's are obtained from the trans- and cis-monomers, respectively. This conclusion suggests the cis-opening mechanism of anionic-type polymerization, and seems to be consistent with the polymerization mechanism suggested by Natta et al. (6) for anionic polymerization.

In the case of cationic-type polymerization, it has been found by

Natta et al. (7) from the results of x-ray studies that the polymers obtained from trans- and cis-β-chlorovinyl ethers have the threo and erythro structures, respectively, and this fact suggests the cis-opening of the double bond. It is interesting that the cis-opening mechanism was concluded in both cases, in spite of the different types of polymerization (anionic and cationic).

The authors express their gratitude to Professor K. Joh and his collaborators for the use of the computer (NEAC 2203) and the helpful suggestions for programming.

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POLYMER LETTERS VOL. 1, PP. 409-411 (1963)

STEREOREGULARITY OF POLYMETHACRYLONITRILE

Methacrylonitrile has been polymerized by various methods, but the stereoregularity of the polymers is not known as yet. The purpose of this note is to report the stereoregularity of methacrylonitrile polymers obtained by n-butyllithium catalyst and by γ-ray irradiation in the solid state.

Since infrared spectrum, NMR spectrum, and x-ray diffraction pattern of polymethacrylonitrile did not reveal stereoregularity, we tried to change polymethacrylonitrile into polymethyl methacrylate, the stereoregularity of which has been made clear by many investigators.

Polymethacrylonitrile was hydrolyzed in a 20% NaOH aqueous solution to give polymethacrylic acid which in turn was esterified to polymethyl methacrylate by diazomethane. The yield of polymethyl methacrylate from polymethacrylonitrile was about 50%. The elementary analysis of the polymethyl methacrylate showed that the ratio of $COOCH_3$ groups to total side groups in the polymethyl methacrylate was about 94%, the rest of the side groups probably being $CONH_2$ groups.

However, the infrared spectrum of polymethyl methacrylate derived from polymethacrylonitrile polymerized by γ-ray irradiation (Fig. 1) was the same as that of methyl methacrylate polymer, except for bands which change by the difference in the stereoregularity.

In order to examine the stereoregularity from the infrared spectrum, the J value of Goode et al. (1) was calculated. The J value of polymethyl methacrylate which was derived from polymethacrylonitrile poly-

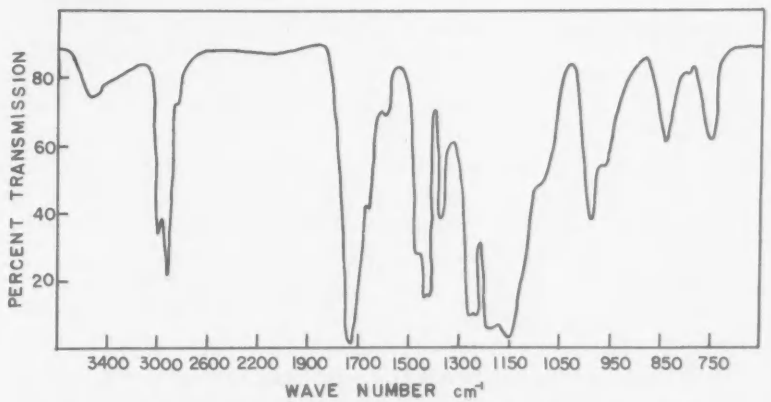

Fig. 1. Infrared spectrum of polymethyl methacrylate derived from polymethacrylonitrile polymerized by γ-ray irradiation at $-78^{\circ}C$.

merized by γ-ray irradiation was 56, which indicates that the polymer has a stereoblock structure.

For polymethacrylonitrile obtained with n-butyllithium catalyst, the J value of polymethyl methacrylate derived was also 56.

To determine the stereoregularity from the NMR spectrum (Fig. 2), the method employed by Bovey et al. (2) was used. As shown in Figure 2, in the NMR spectrum of polymethyl methacrylate which was derived from polymethacrylonitrile polymerized by γ-ray irradiation, there are two peaks, at 8.78 and 8.98 τ, due to α-CH_3 groups of monomer units, which are attributed to isotactic and heterotactic configurations, respectively. And this spectrum has no absorption due to syndiotactic configurations. This indicates that the polymer has stereoblock structure, conforming with the result from the infrared spectrum.

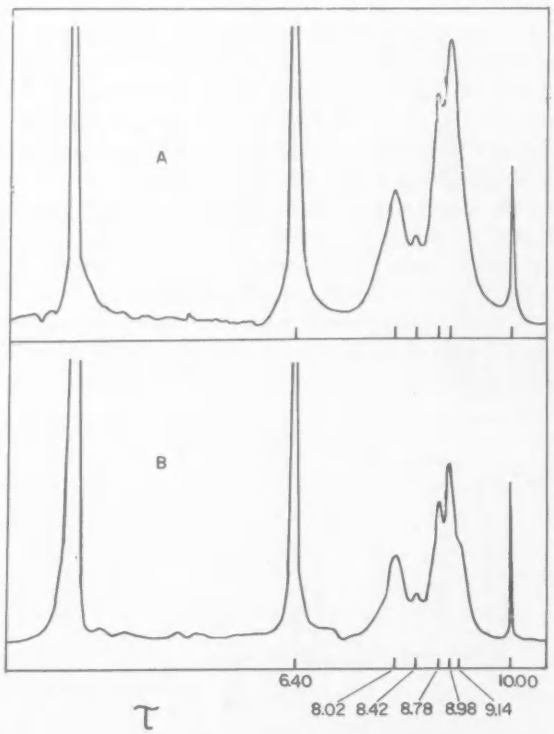

Fig. 2. NMR spectra of (A) polymethyl methacrylate derived from polymethacrylonitrile polymerized by γ-ray irradiation at $-78°$C. and (B) that from polymethacrylonitrile polymerized with n-butyllithium catalyst (10% solutions of the polymers in chloroform with tetramethylsilane reference).

There are three peaks, at 8.78, 8.98, and 9.14 τ, in the NMR spectrum of polymethyl methacrylate which was derived from polymethacrylonitrile prepared with n-butyllithium initiator.

To determine the proportions of isotactic, heterotactic, and syndiotactic configurations, the areas of individual peaks were estimated.

The stereoregularity of polymethyl methacrylate, and consequently of the starting polymethacrylonitrile, is shown in Table I.

TABLE I

Stereoregularity of Polymethacrylonitrile

Polymer no.	Polymerization conditions of polymethacrylonitrile	IR	NMR		
		J value	i (%)	h (%)	s (%)
1	γ-ray, at −78°C. (solid state), in bulk	56	36	64	0
2	n-Butyllithium catalyst, at −78°C., in toluene solution	56	32	55	13

From the data of Table I the stereostructure of polymethacrylonitrile polymerized by γ-ray seems to be DDDLLLDDDLLL, if the stereostructure of the polymers is not different between the polymer molecules and is uniform in a molecule.

Investigations of the stereoregularity of methacrylonitrile polymers obtained with other catalysts are in progress.

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POLYMER LETTERS VOL. 1, PP. 413-414 (1963)

AN EXPLANATION REGARDING THE INITIATION OF THE POLYMERIZATION OF N-VINYLCARBAZOLE IN CARBON TETRACHLORIDE

Two recent reports describe the formation of a yellow color and a spontaneous polymerization of N-vinylcarbazole when this monomer is mixed with a comparatively small amount of carbon tetrachloride (1,2). Chapiro and Hardy postulated a free radical mechanism for this polymerization (1); Breitenbach and Srna confirmed the experimental results, but suggested that a cationic mechanism is involved, since methylmethacrylate failed to copolymerize when it was added to the reaction mixture (2).

We have recently reported (3) a cationic polymerization of N-vinylcarbazole catalyzed by a variety of oxidants such as halogens, nitrogen oxides, quinones, and tetracyanoethylene, suggesting that the polymerization is initiated by the Wurster ion of N-vinylcarbazole formed by oxidation of monomer. Almost all of the compounds used as catalysts are known to react with aromatic amines to yield Wurster ions as principal products or as secondary products following charge-transfer complex formation, and Wurster salts of aromatic amines also catalyze this polymerization. This is believed to be the first reported example of a radical-cation initiated addition polymerization.

One of the methods by which the chlorine catalyzed polymerization was studied involved using a reagent grade of 1,1,2,2-tetrachloroethane obtained from the Eastman Kodak Co. A yellow color can be observed to form when N-vinylcarbazole is mixed with a comparatively small amount of this solvent. The ultraviolet absorption spectra of dilute solutions of N,N'-tetramethyl-p-phenylenediamine and 1,4-diaminodurene in this solvent were found to be the same as those of the Wurster ions of these amines (4,5). Similar effects were observed when traces of chlorine were added to solutions of these amines in reagent grade methylene chloride. The ultraviolet absorption spectra of these amines in methylene chloride remained unaffected by the addition of traces of hydrogen chloride, and thus the effect of 1,1,2,2-tetrachloroethane on the absorption spectra of aromatic amines cannot be attributed to the possible presence of hydrogen chloride.

In light of these experiences with chlorinated solvents, we investigated whether N-vinylcarbazole polymerizes in carbon tetrachloride free of chlorine. We find carbon tetrachloride to be an inert solvent under these conditions. The reported yellow color forms and polymerization occurs, however, when a trace of chlorine is added to the monomer solution. It is believed, therefore, that the polymerization of N-vinylcarba-

zole in certain types and grades of chlorinated solvents is due to the presence of a trace of an oxidant such as chlorine. It is also of interest that chlorine will catalyze the polymerization of solid N-vinylcarbazole in the absence of solvent. The observation of Breitenbach and Srna (2) that methylmethacrylate does not copolymerize with N-vinylcarbazole is consistent with our report (3) that styrene and acrylonitrile can serve as inert solvents for the polymerization of N-vinylcarbazole catalyzed by chlorine and other oxidants.

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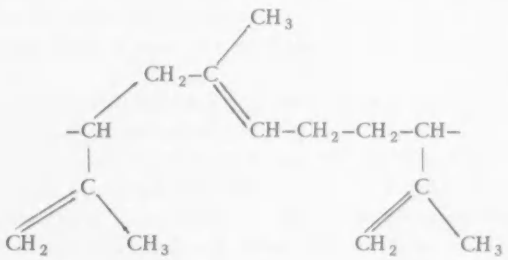
POLYMER LETTERS VOL. 1, PP. 415-417 (1963)

INFRARED SPECTRA AND ANALYSES OF SYNTHETIC POLYISOPRENES

Studies of the infrared spectra of synthetic polyisoprenes have led to the conclusion that the I.R. spectra of polymers containing cis-1,4, trans-1,4, and 3,4- or cyclic structural units are not additively composed of the spectra of stereoregular polymers containing only one of these structures.

It is known that stereoregular cis-1,4-polyisoprene (hevea) and stereoregular trans-1,4-polyisoprene (balata) have absorption bands at 1130 and 1150 cm.$^{-1}$, respectively. It has been found that a polymer having a high content of 3,4- structural units, in addition to the 1,4- structural units, has no absorption band at either 1130 or 1150 cm.$^{-1}$ but does have a band at 1140 cm.$^{-1}$ (Fig. 1). We attribute this band to the C–CH_3 vibration of the –C(CH_3)=CH– structural unit separated by other structural units.



The appearance of the absorption band at 1140 cm.$^{-1}$ in some synthetic polyisoprenes has been mentioned several times by Binder (1-3) with the comment that the origin of this band is not known (3).

A similar phenomenon has been discovered by analysis of a polymer having approximately 20% trans-1,4 in addition to about 75% cis-1,4 structural units, as estimated by an analysis (4) using the absorption bands at 572 and 980 cm.$^{-1}$. In this polymer no absorption band appeared at 1150 cm.$^{-1}$ and the wave number of the band at 1130 cm.$^{-1}$ was shifted towards higher values. In a mixture of hevea and balata with the same content of 20% trans-1,4- structural units both the 1130 and 1150 cm.$^{-1}$ bands are quite distinct (Fig. 1).

The behavior of the 1130 and 1150 cm.$^{-1}$ bands is in agreement with the finding of Golub (5) who has shown that during the cis-trans isomerization of polyisoprene the 8.80 μ absorption band appears instead of the 8.88 μ band in cis-1,4 isomers or the 8.70 μ band in trans-1,4 iso-

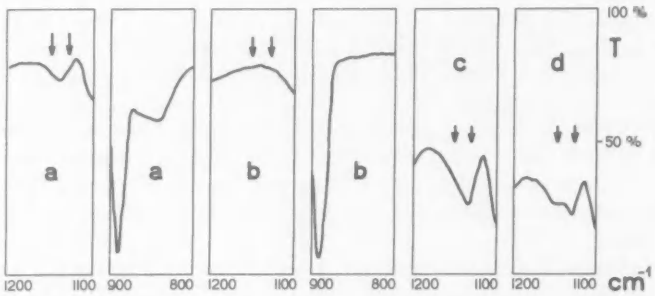


Fig. 1. Infrared spectra of polyisoprene in CS_2: (a) 0.5% solution of polyisoprene with 3,4- and 1,4- structural units; (b) 0.5% solution of 3,4-polyisoprene (6); (c) 3% solution of polyisoprene with approximately 20% trans-1,4 structural units; (d) 3% solution of a mixture of 80% hevea and 20% balata.

mers. The statement of Binder (3) that the small amount of trans-1,4 structural units may be better detected using the band pair near 7.65 μ rather than the bands at 8.84 and 8.68 μ is also in good agreement with our findings.

As a consequence of our results and those of the other workers, it is possible to conclude that only polyisoprenes having long sequences of cis-1,4 or trans-1,4 units have the absorption bands at 1130 and 1150 $cm.^{-1}$, respectively. It is also evident that the analysis of synthetic polyisoprenes using these absorption bands leads to distorted results. We have obtained better results using the absorption bands at 572, 980, and 888 $cm.^{-1}$ for cis-1,4, and trans-1,4, and 3,4-polyisoprene structural units, respectively. The use of various combinations of different absorption bands permits one to conclude whether a polymer in question is more of the block copolymer type or a mixture of stereoregular polymers (4).

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POLYMER LETTERS VOL. 1, PP. 419-421 (1963)

CRYSTAL STRUCTURES OF MONOMERS POLYMERIZABLE IN THEIR SOLID STATES. PART I. ACRYLIC ACID

Solid state polymerizations recently developed by many workers are very attractive from many points of view (1). In cyclic monomers, such as trioxane, diketene, and β-propiolactone, it was found that highly ordered products could be obtained by solid state polymerizations, indicating that directions of chain growings are surely controlled by the geometry of each monomer crystal lattice (2). On the other hand, e.g., vinyl monomers, production of crystalline polymer by solid state polymerization has not yet succeeded, and thus some different views on the role of crystal structures of monomers have been proposed. However, it appears that information about the crystal structures of vinyl monomers is insufficient to come to a definite conclusion about the role of crystal structures of monomers. We have been studying the crystal structures of some vinyl and cyclic monomers, and in this letter we will report on the x-ray structure analysis of acrylic acid.

Reagent-grade acrylic acid was separated from inhibitor by vacuum distillation with copper powder to inhibit polymerization. Single crystals in long prisms, as shown in Figure 1, were obtained by keeping the substance slightly below its melting point (11°C.). Three-dimensional x-ray data were obtained at –70°C.. The unit cell dimensions derived from rotation and Weissenberg photographs are a = 11.66, b = 10.10, and c = 6.38 A. There are eight molecules per unit cell, and the space group was found to be D_{2h}^{26} – Ibam. Figures 2 and 3 show the molecular dimensions and the crystal structure of acrylic acid, respectively. The atomic coordinates are listed in Table I. The planer molecules are arranged on the planes at z = 0 and 1/2, and hydrogen bonds (2.65 A.) connect pairs

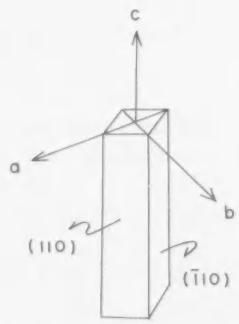

Fig. 1. Single crystal of acrylic acid.

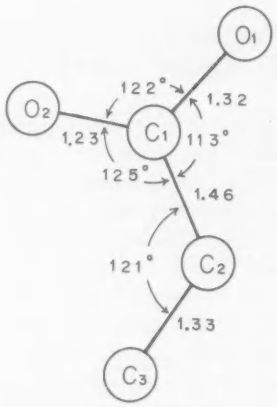

Fig. 2. Molecular dimensions of acrylic acid.

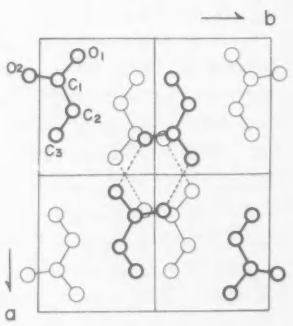

Fig. 3. Crystal structure of acrylic acid. Molecules drawn by thick lines and thin lines are arranged on the planes at z = 0 and 1/2, respectively. The hydrogen bonds are shown by broken lines.

TABLE I

Atomic Fractional Coordinates and Temperature Factors[a]

	x	y	z	$B_1(A^2)$	$B_2(A^2)$
O_1	0.0637	0.1667	0	1.0	4.2
O_2	0.1353	0.0397	0	1.0	4.2
C_1	0.1493	0.0816	0	1.3	4.4
C_2	0.2610	0.1460	0	1.3	5.0
C_3	0.3571	0.0751	0	1.9	5.8

[a] Thermal vibration correction was made by the expression, $\exp -1/4 [B_1(h^2/a^2 + k^2/b^2) + B_2 l^2/c^2]$.

of the molecules into centrosymmetrical dimers. The Van der Waals contacts are normal; the shortest $C(H_2)\cdots\cdots C(H_2)$ distance is 3.52 A. and the $C(O)\cdots\cdots O$ distance is 3.21 A. Furthermore, the cleavage planes are found to be parallel to the molecular planes.

According to the data of Mesrobian et al., γ-irradiated polymerization of acrylic acid in the solid state proceeds fast (3). From the measurement of ESR spectrum of the single crystal by Shioji et al., it was found that free radicals induced by exposure to ionizing radiation are frozen at $-196°$C. and are of the $CH_3-\dot{C}H-COOH$ type. Furthermore, referring to the molecular orientation of acrylic acid in the crystalline lattice presented in Figure 3, it was found that the radicals were oriented in the crystalline lattice in the same way as in the undamaged molecules (4). A detailed study on the propagation of polymerization and the nature and the structure of polyacrylic acid produced by the solid state polymerization still remains an open question.

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DENSITY OF POLYACRYLONITRILE

The density of polyacrylonitrile (PVCN) fibers has been reported many times in the current literature (1, 3-7). The maximum value reported in all of these papers is slightly less than 1.200, which is in harmony with the maximum values from many hundreds of determinations made in this laboratory on both acrylonitrile homopolymers and copolymers containing at least 85% acrylonitrile by weight.

Several of the above-listed papers contain references to an article by Stefani (2) in which the density of PVCN is given as ranging from 1.17 to 1.22 (1, 3, 5). The values in Stefani's paper were based on data reported by Rein in 1949 (8). Rein's results are apparently based on work done prior to 1943 at I. G. Farben. He makes no reference concerning techniques employed to obtain density, or any estimate of the accuracy of the method. To convey a clearer idea of the data, his table of specific gravities is given in Table I.

TABLE I

Specific Gravity of Fibers According to Rein

Polyacrylonitrile	1.17-1.22
Nylon, PERLON	1.14-1.21
Protein fibers	1.3
Polyvinylchloride fibers	1.4
Cellulose fibers	1.5
Polyvinylchloride 120 (SARAN)	1.65
Glass Fibers	2.5

In view of the presumably more accurate work done in recent years, and also of the work in this laboratory, the authors feel Rein's density range for PVCN should be considered as only approximate, and specifically that the 1.22 datum is in error.

Unusually high densities have been obtained in this laboratory for PVCN, but never as the oriented dried fiber. Wet spun, unstretched polyacrylonitrile gelled filament, when never dried or heated above 50°C., gives a density of approximately 1.235 g./ml. These determinations were made in the following manner.

A solution containing 10% by weight of Orlon 42 dissolved in an aqueous solution of 60% zinc chloride was spun into an aqueous bath contain-

ing 42% zinc chloride at 15°C. The gelled filament was washed free of zinc chloride with distilled water. The never-dried filament was next steeped in acetone to remove the water, then placed in a 50%, by volume, solution of n-heptane and carbon tetrachloride. These filaments were floated in a density gradient column of n-heptane-carbon tetrachloride at 25°C. The results of a number of density determinations are given in Table II.

TABLE II

Densities of Polyacrylonitrile (g./ml. at 25°C.)

	Experimental polyacrylonitrile homopolymer	Copolymer[a]
a. Washed, unheated unstretched filament	1.2323	1.2368
b. (a) above, after 2× stretch in water at 25°C.	1.2257	1.2235
c. (a) after heating 15 sec. in boiling water	1.1890	1.1732
d. (a) dried at 120°C. in a hot air oven	1.1785	1.1856
e. (a) stretched 8× in boiling water	1.2032	1.1895
f. (e) dried at 120°C. in a hot air oven	1.1769	1.1878

[a] Orlon 42 acrylic dissolved in aqueous 60% zinc chloride.

The fact that freshly coagulated filaments have a high polymer density is in itself very unusual. Wet coagulation under the conditions described must permit access of surrounding liquid to essentially all space between the polymer aggregates. It is during heating that voids develop, and these voids must be almost totally inaccessible to interstitial liquid. This was shown in the following way.

Coagulated, washed filaments were heated in (a) glycerine, density$_{20°}$, = 1.260 g./ml., and (b) mineral oil (Nujol), density$_{20°}$, = 0.778 g./ml. after interstitial water had been replaced with the liquid indicated. (In the case of Nujol, it was necessary to replace water with acetone, and the acetone with n-heptane before Nujol could be introduced.) Results are summarized in Table III.

TABLE III

Densities of Polyacrylonitrile After Heating in Various Media

Filament heated in	At	Experimental homopolymer	Copolymer[a]
a. Water	100°C.	1.1890	1.1732
b. Glycerine	120°C.	1.1978	1.2008
c. Nujol	130°C.	–	1.1825

[a] Orlon 42 acrylic dissolved in aqueous 60% zinc chloride.

Were interstitial liquid trapped in the polymer during polymer rearrangement in heating, the density of the filament would be a sensitive function of the density of the liquid in which it was heated. Such is not the case.

The high density of freshly coagulated filament is not due to preferential diffusion of carbon tetrachloride into the gel structure in the n-heptane-carbon tetrachloride density gradient tube. This was shown by placing the coagulated filament in formic acid (density$_{20°}$ = 1.220 g./ml.) or nitrobenzene (density$_{18°}$ = 1.205). In each liquid, unheated filament sank, and the filament heated to 100° in water floated. (Before immersion in nitrobenzene, water was removed with acetone.)

Thus the void structure which develops upon heating coagulated polyacrylonitrile must be contained within the polymer matrix, and these voids must be inaccessible to the surrounding liquid. For this to be true it seems likely that these voids are extremely small.

Thus the voids in wet spun commercial acrylic fibers do not have their primary origin in lack of perfect fit of oriented microfibrils upon drying and fibrillar compaction. Rather, most of the void volume exists within the polymer matrix after heating and prior to drawing.

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RADIATION-INDUCED SOLID STATE POLYMERIZATION OF TETRAOXANE

The authors have previously reported the radiation-induced low temperature polymerization of formaldehyde to high molecular weight polyoxymethylene (1,9), and also the formation of oriented polyoxymethylene by the solid state polymerization of trioxane (2-6). In this communication, the radiation-induced polymerization of tetraoxane, the cyclic tetramer of formaldehyde, is reported and compared with that of trioxane.

Tetraoxane was obtained by the thermal decomposition of acetylated paraformaldehyde (10) and recrystallized from carbon disulfide to crystals 3 mm. long and 1 mm. thick. Cobalt 60-γ rays were used as the radiation source. After the irradiation, unreacted monomer was removed by extraction with acetone and the polymer yield was obtained by weighing after vacuum drying. The x-ray diffraction analysis was carried out using a Shimazu GX-II type diffractometer.

Tetraoxane, a solid which can be sublimed, melts at 112°C. No report was found on its polymerizability even by a catalyst. Under the irradiation of γ-rays, e.g., at 80°C. at a dose rate of 2.5×10^4 r./hr. the crystal became gradually opaque (Fig. 1). After 18 hr. irradiation a polymer crystal with the shape of the monomer crystal was obtained at 94% conversion. However, no polymer was obtained in the melt or in solution. The polymer yield is shown in Table I as a function of irradiation dose and temperature. The polymerization proceeded at a considerably large rate. The conversion was linear during irradiation and was completed after 20 hr. irradiation at 80°C. This rate of polymerization was much larger than the maximum rate for trioxane at 55-60°C. A conversion of 100% was easily attained compared to the difficulty in the polymerization of trioxane where a yield of 70-80% was attained only in larger

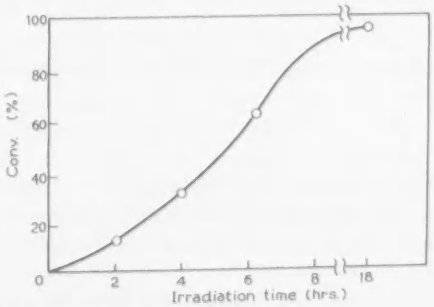

Fig. 1. Radiation induced solid state polymerization of tetraoxane. Polymerization at 80°C., $I = 2.5 \times 10^4$ r./hr.

TABLE I

Radiation Induced Solid State Polymerization of Tetraoxane
(In-Source Polymerization)

Expt. No.[a]	Temp., °C.	I, 10^4 r./hr.	T, hr.	D, 10^5 r.	Conv., %
1	55	2.5	4.0	1.0	<1
2	55	2.5	8.0	2.0	<1
3	60	2.5	8.0	2.0	<1
4	80	2.5	2.0	0.5	12
5	80	2.5	4.0	1.0	31
6	80	2.5	6.2	1.5	61
7	80	2.5	18.1	4.5	94
8	100	2.5	4.0	1.0	85

[a]Irradiation in air.

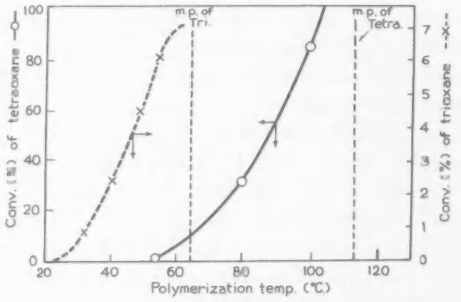

Fig. 2. The influence of temperature on the rate of solid state polymerization of tetraoxane in comparison with trioxane (in source polymerization). (O) Tetraoxane, I: 2.5×10^4 r./hr., D: 1.0×10^5 r.; (X) trioxane, I: 1.1×10^4 r./hr., D: 1.0×10^5 r. Crystal size: 3mm. × 1mm. ϕ in both tetraoxane and trioxane.

crystals. The temperature dependence of the polymerization rate is shown in Figure 2. The temperature range for tetraoxane polymerization was 55 to 112°C. and at 100°C. a 90% polymer yield was obtained with a dose of only 1×10^5 r.

Although it is very difficult to compare the rate of solid state polymerization of two monomers having different melting points and phase transition points (the rate of solid state polymerization depends on the crystalline state), it was obvious that tetraoxane had a wider temperature range than trioxane (25-64°C.) and the former polymerized more easily at the same temperature interval below the melting point.

The G-values for monomer disappearance in the two monomers at the

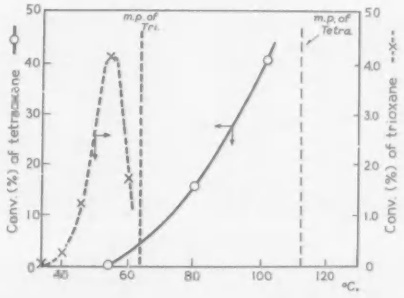

Fig. 3. The influence of temperature on the rate of solid state polymerization of tetraoxane in comparison with trioxane (post-polymerization). (O) Tetraoxane, I: 1.8×10^4 r./hr., D: 1.1×10^5 r.; (X) trioxane, I: 2.2×10^4 r./hr., D: 1.1×10^5 r. (post-polymerization, 6 hr. in both).

TABLE II

Radiation Induced Solid State Polymerization of Tetraoxane (Post-Polymerization)

	Pre-irradiation				Post-polymerization		
Expt. No.[a]	Temp., °C.	I, 10^4 r./hr.	T, hr.	D, 10^5 r.	Temp., °C.	T, hr.	Conv., %
10	–78	1.8	6.2	1.1	55	6.0	~0
11	–78	1.8	6.2	1.1	80	6.0	15
12	–78	1.8	6.2	1.1	100	6.0	40
13	80	2.5	18.1	4.5	100	1.0	99
14[b]	–78	1.8	6.2	1.1	80	6.0	74

[a]Irradiation and polymerization in air.

[b]Irradiation and polymerization in vacuum.

maximum rate of polymerization were, G (tetraoxane), 7×10^4 (100°C.) and G (trioxane), 6×10^3 (55°C.).

Figure 3 and Table II show the temperature dependence of post-polymerization of tetraoxane in comparison with that of trioxane. It was observed that tetraoxane post-polymerized in the solid state just as trioxane did, and that the rate of the reaction had a high temperature coefficient.

Experiment 13 indicates that post-polymerization is possible even with irradiation at 80°C. Further study is necessary to clarify the polymerization mechanism of this monomer. A cationic mechanism was expected and this assumption is supported by mass spectrometry. The

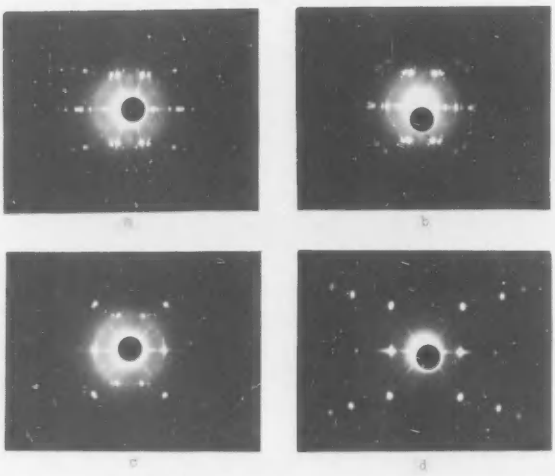

Fig. 4. Rotation x-ray diffraction diagrams of monomer (tetraoxane), irradiated monomer and polymer (polyoxymethylene) in source polymerization at 80°C. (a) Monomer; (b) conv., 20%, D = 5.2×10^4 r.; (c) conv., 50%, D = 1.3×10^5 r.; (d) polymer.

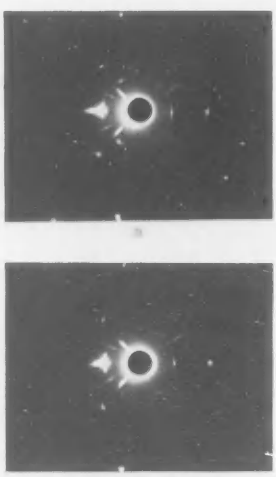

Fig. 5. X-ray diffraction diagrams of polytetraoxane at various relative angle of rotation around the fiber axis. Polymer: polymerized at 60°C., conv., 99%; (a) relative angle 0°; (b) relative angle 60°.

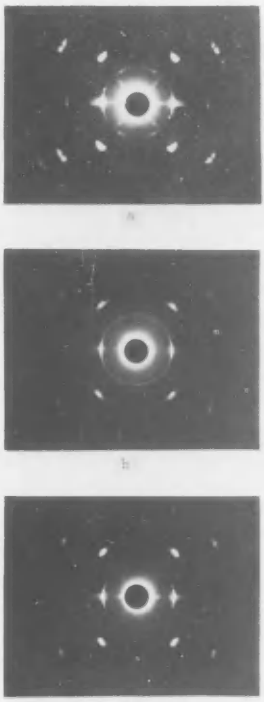

Fig. 6. Rotation x-ray diffraction diagrams of polytetraoxane from various polymerization temperature. (a) Polymerized at 60°C., conv., 99%; (b) polymerized at 80°C., conv., 61%; (c) polymerized at 100°C., conv., 85%.

positive ions of mass number 31 and 61 were observed in the mass spectrometry of tetraoxane, as well as in trioxane. Below are suggestions of the species which may initiate the polymerization in the solid state (7).

m/e	31	61
	$HOCH_2^+$	$HOCH_2OCH_2^+$

Figure 4 shows the change in the x-ray diffraction diagram of tetraoxane crystal during polymerization, in which the diagram characteristic of the polymer crystal overlapped that of the monomer just as in the case of trioxane.

Figure 5 shows that an oscillation in the x-ray diffraction diagram is unsymmetrical and has a periodicity of 60°. It may be concluded that the polytetraoxane crystal exhibits three-dimentional order.

The effect of polymerization temperature on the polymer crystal structure is shown in Figure 6 in which almost no twin configuration spots were observed, especially at higher temperature, in contrast to the clear twin crystals of polytrioxane (4). This may mean that epitactic polymerization depends on the monomer crystal structure, since tetraoxane is monoclinic (8) while trioxane is hexagonal. A more detailed study is now in progress.

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THE "ZERO POINT" FOR THE Q,e SCHEME

Several recent papers (1-3) have pointed out the necessarily somewhat arbitrary nature of the assignment of e values in our Q,e scheme (4) and suggested an alternative choice for the "zero point." Our choice of $e = -0.8$ for styrene placed vinyl chloride at $e \sim 0$. Kawabata, Tsuruta, and Furukawa (1) have proposed a choice of $e = 0$ for styrene and Bamford and Jenkins (2), by proposing the benzyl radical as reference, in essence make the same choice. Burkhart and Zutty (3) have determined the e value for ethylene on our scale as −0.4, but suggest that ethylene should be used as the reference monomer and assigned $e = 0$.

In the case of Hammett's σ,ρ scheme (5) the arbitrary necessity of picking a reference point was resolved very satisfactorily by choosing $\sigma = 0.0$ for hydrogen. However, for the Q,e scheme one cannot be quite so freely arbitrary in one's choice, because the Q,e scheme involves an estimate of both electrical and resonance energy terms additive to the activation energy (4), whereas the Hammett equation involves essentially only an additive electrical term (6). Thus a choice of different reference "zero points" for the Q,e scheme involves considerable changes of even the relative resonance terms (Q) for negative and positive substituents since an incorrect choice in effect puts part of the electrical energy in with the resonance term. The choice is therefore clearly not as freely arbitrary as for the Hammett σ,ρ scheme and, in fact, this was the reason for our adjustment from the original assignment of $e = -1.0$ (4a) to $e = -0.8$ (4b, c). The linear correlation between the Q of Kawabata, Tsuruta, and Furukawa (1) and Hammett's σ constant would seem to suggest that they have included a substantial fraction of the polar factor into their Q (based on $e = 0$ for styrene).

An examination of bond moment data seems to support our assignment of $e = -0.8$ for styrene ($e \sim 0$ for vinyl chloride) rather than $e = 0$ for styrene (1, 2) or for ethylene (3). The bond moment for the carbon-hydrogen bond ($\mu = 0.3$D) (6) can be interpreted in terms of a charge of −0.28 e.s.u. on carbon and +0.28 e.s.u. on hydrogen.* Thus, in ethylene the accumulation of negative charge on the double bond carbons would be −1.12 e.s.u. The carbon-chlorine bond moment ($\mu = 1.6$D) can be interpreted as placing a charge of +0.9 e.s.u. on carbon and −0.9 e.s.u. on chlorine. Thus in vinyl chloride, the net charge on the double

*The calculations of Coulson (7) indicating that an isolated σ bond constructed from an sp^3 orbital on carbon and an s orbital on hydrogen would have moment with its positive end toward carbon has been widely misinterpreted as supporting opposite polarity for the carbon hydrogen bond because the very large dipole moment of the sp^3 orbital itself is overlooked.

bond carbons would be +0.06 e.s.u., i.e., very nearly zero.

The bond moments above are derived from saturated carbon (sp^3) compounds. An olefinic or free radical carbon (sp^2) would have a greater electron affinity (8) and would therefore have even more negative charges on carbon than estimated above. It may therefore be concluded that ethylene should definitely have a considerable negative value for e, that vinyl chloride should be very near the true zero point and that our assignment of e = –0.8 for styrene is approximately correct.

The fact that the revised Q values of Kawabata, Tsuruta, and Furukawa and Szwarc's methyl radical affinities are parallel is not a valid argument against the conclusion that e = –0.8 for styrene is correct. One would expect the methyl radical to have an electrical factor very similar to the styryl radical and therefore their relative reactivities should be parallel.

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EXPLOSIVE DECOMPOSITION OF A MIXTURE OF ETHYLENE AND CHLOROTRIFLUOROETHYLENE IN A Co^{60} GAMMA RADIATION FIELD*

An interesting observation, made during the study of the copolymerization of the ethylene-chlorotrifluoroethylene system by gamma radiation, was the explosive spontaneous decomposition of the components at certain radiation conditions.

Experimental

Irradiations were performed in stainless steel reaction vessels designed to operate at a maximum pressure of 1000 atm. The upper assembly of the vessel contains a closure valve and a rupture disc set to burst at 14,000 psi. The lower assembly contains a thermocouple well for measuring reaction temperatures.

The ethylene gas used was supplied by Phillips Petroleum Co., containing <5 ppm O_2. The chlorotrifluoroethylene was from the Matheson Co. having 50 ppm O_2. The concentration of O_2 in the CTFE was reduced to ≈5 ppm by distillation on a vacuum rack.

A measured amount of CTFE was introduced into the reaction vessel by condensing with liquid N_2. After warming to room temperature, ethylene gas was introduced into the vessel through a compressor to a total pressure of 10,000 psi.

Irradiations were conducted in a variable source jig in the BNL gamma pool facility at ambient temperatures (18-20°C.).

Results and Discussion

Table I shows the experimental conditions and the results obtained in a number of runs in which both the initial concentration of monomers and the dose rate were varied.

The first experiment of the series, shown in Table I, having an initial ethylene/CTFE mole ratio of 29.1:1, was irradiated at a dose rate of 230,000 rad./hr. and room temperature. Polymerization at these conditions proceeded normally to a total dose of 16.2×10^6 rad.

A second experiment, prepared in a similar way, and having an ethylene/CTFE mole ratio of 11.9:1, was irradiated at a higher dose rate of 308,000 rad./hr. After a total dose of ≈50,000 rad., the system exploded violently (the rupture disc was broken) with the formation of a considerable quantity of carbon black.

*Work Performed Under the Auspices of the U. S. Atomic Energy Commission, Division of Isotope Development.

TABLE I

Co^{60} Gamma Copolymerization of Ethylene and Chlorotrifluoroethylene

Run no.	Intensity, rad./hr.	Dose, 10^6 rad.	Ethylene, g.	CTFE, g.	Initial mole ratio, E/CTFE
20–0	230,000	16.2	49.0	7.0	29.1
20–1	308,000	0.05[b]	45.0	15.7	11.9
20–2	308,000[a]	0.92	–	15.4	–
20–3	308,000	0.04[b]	49.0	7.0	29.1
20–4	216,000	0.50	49.0	7.3	28.0
20–6	300,000	1.2	55.8	2.6	89.37
20–7	300,000	1.2	55.0	5.0	45.78
20–8	300,000	0.023[b]	50.8	7.5	28.17

[a] Pure CTFE polymerization.

[b] Total dose at which explosive decomposition occurred.

Another explosive reaction at the same dose rate occurred when the initial concentration of CTFE was reduced approximately 2½ times (run #20–3). Additional experiments at 300,000 rad./hr. were made in which the initial concentration of ethylene to CTFE was varied (runs #20–6, 20–7, 20–8). A violent explosive reaction occurred when an ethylene/CTFE mole ratio similar to that of run #20–3 was used. Pure chlorotrifluoroethylene, irradiated at a dose rate of 308,000 rad./hr. polymerized to form a solid white polymer.

In previous work on the γ-ray induced polymerization of ethylene (1) at dose rates to 900,000 rad./hr. and pressures to 10,000 psi an explosive reaction never occurred.

It appears from the data in Table I, that both the concentration of CTFE and the dose rate play a role in initiating the explosion. Further study, however, is necessary to determine the critical conditions involved in initiating the decomposition of this system in a radiation field.

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POLYALDEHYDES

The polymerization of aldehydes employing organometallic compounds and Lewis acids as catalysts has received considerable interest in recent years. Bevington has recently made a review of the developments in this field. The polymerization of unsaturated aldehydes is mentioned, and it is indicated that such aldehydes polymerize, but generally the reactions involve the ethylenic-double bond rather than the carbonyl bond (1). Also, Koral has recently reported the polymerization of crotonaldehyde by means of certain tertiary phosphines to a vinyl-type polymer (2).

We wish to report some data concerning the polymerizability of unsaturated aldehydes and also to relate the formation of some previously unpublished polyaldehydes. The polymerizations were conducted at −78°C. in n-hexane under an inert atmosphere of nitrogen employing aluminum triethyl as a catalyst. Hydrocinnamaldehyde, cyclohexanecarboxaldehyde, and 3-cyclohexene-1-carboxaldehyde polymerized readily under these conditions. Benzaldehyde, crotonaldehyde, cinnamaldehyde, and furfuraldehyde are examples of α,β-unsaturated aldehydes that did not polymerize under the above described conditions.

The polymers obtained directly from the reaction mixtures were thermally unstable, as is true of all polyaldehydes. The infrared spectra of these materials indicated no carbonyl functionality but strong absorption was observed in the acetal region. In all three cases, the polymers were crystalline as evidenced by x-ray diffraction studies.

This is believed to be the first report of high molecular weight crystalline polymers of the above-mentioned aldehydes, the first polymerization of alicyclic aldehydes to high polymers, and the first high molecular weight crystalline polymer involving the carbonyl bond of an unsaturated aldehyde.

These data indicate that unsaturation conjugated with the carbonyl group is detrimental to polymerization reactions involving the carbonyl group. This is evident from the ease of polymerization of the corresponding saturated aldehydes as compared to the lack of polymerization of the α,β-unsaturated aldehydes. Furthermore, nonconjugated unsaturation appears to have no effect on polymerizability as evidenced by the formation of poly(3-cyclohexene-1-carboxaldehyde). It is probable that the electrophilic character of the carbon atom of the carbonyl group is decreased to such an extent in the α,β-unsaturated aldehydes studied, that coordination with the catalyst does not occur. The lack, or at least difficulty, of ketone polymerizations would seem to substantiate this observation.

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CRYSTALLINITY OF POLYETHYLENE AS STUDIED BY THERMOLUMINESCENCE

Our previous experiments on the thermoluminescence of polyethylene irradiated with gamma rays at liquid nitrogen temperature and in the absence of oxygen, revealed three distinct peaks in the "exponential" glow curve (1). These three peaks (α, β, γ) appear to be related to crystallinity, α being most prominent with polyethylene of high density (high crystallinity) and with straight chain paraffins. Low density (branched polyethylene) gives relatively much larger β and γ peaks. The importance of crystallinity is not, however, proven since the low density polyethylene may show larger β and γ peaks because of the higher degree of chain branching.

In the presence of oxygen the β and γ peaks are removed and replaced by a new ϵ peak intermediate between the α and previous β peak (2). This ϵ peak can be removed by pre-irradiation and warming in order to combine the oxygen molecules initially present in the sample with alkyl radicals formed by the pre-irradiation. The peroxide radicals produced in this way do not participate in subsequent thermoluminescence reactions so this treatment leaves the specimen effectively free of oxygen. Subsequent irradiations then produce the α, β, γ system typical of irradiations in the absence of oxygen.

Single crystals of polyethylene can be formed by crystallization at 70°C. from a 1% xylene solution (3). This offers the possibility of comparing samples of polyethylene which are chemically identical but of different degrees of crystallinity.

Experimental

The following samples were available:

(a) Single polyethylene crystals prepared by Dr. A. Keller.

(b) Similar crystals which after preparation had been fused under vacuum.

(c) Bulk (commercial Marlex 50) polyethylene granules as used in the preparation of (a) and (b).

All these samples were sealed in suitable glass tubes in the presence of air and were given the usual pre-irradiation and warming to remove any molecular oxygen. They were then irradiated with a standard Co^{60} gamma dose of 0.15 Mrads at liquid nitrogen temperature, allowed to warm up, and the glow curve was recorded using the technique described in our previous papers. The samples were investigated in air since the poor thermal conductivity of an evacuated powder gives considerable

Fig. 1. Exponential glow curves of Marlex 50 irradiated at −196°C. in air with 0.15 Mrad gamma doses. α, ϵ, β, γ peaks from left to right in figure. (i) Bulk Marlex 50 (sample (c); (ii) single crystals (sample a) after pre-irradiation dose; (iii) as in (ii) after further irradiation dose; (iv) fused single crystals (sample b); (v) sample a after being fused. (Thermoluminescence intensities not drawn accurately to vertical scale due to different optical absorptions of different samples.)

temperature variations across the sample during warming in the glass tube.

After completion of the above runs, sample (a) was evacuated and fuzed and then placed in another tube prior to a second irradiation (after a second pre-irradiation treatment). Removal from the first tube was necessary since the fused specimen sticks to the glass and cannot be moved to the other end of the tube after irradiation for examination as required (1).

Results

The glow curves are shown in Figure 1 (i-v).

(i) is the glow curve for the Marlex 50 granules. The usual α, β, γ system is observed. A trace of the ϵ peak is noticeable. This is often found in high density polyethylene and indicates that some uncombined oxygen still remains in the pre-irradiated sample in relatively inaccessible sites.

(ii) shows the glow curve for the single crystals, (sample (a)) after a pre-irradiation dose of 0.15 Mrads. There is little evidence of the ϵ peak, since the material was only exposed to air for a very short period, and being so crystalline absorbs little oxygen in any case.

(iii) shows the corresponding glow curve for sample (a) after a second radiation dose of 0.15 Mrads. In both (ii) and (iii) the β and γ peaks have almost disappeared.

(iv) is the glow curve for the single crystal sample (b), fused in vacuum. In this case the β and γ peaks are again very prominent.

(v) gives the glow curve for sample (a) after it had been fused in vacuum over a Bunsen. Here again the β and γ peaks have reappeared.

It can be concluded that the crystallinity of these specimens rather than the degree of branching, does in fact determine the relative importance of the α and of the β, γ peaks, since the degree of branching in the polymer chains is unaffected by fusing. Indirectly it confirms the expected highly crystalline character of sample (a).

It will be noted that the relative importance of the γ and β peaks appears to change, indicating that these two peaks have somewhat different origins, but the actual cause is not yet clear.

We would like to record our appreciation to Dr. A. Keller both for his gift of single crystals and for many valuable discussions.

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A THEORY OF THE GLASS TRANSITION

The question as to whether the glass transition is of kinetic or of equilibrium origin is of fundamental importance, and has been discussed at great length (1-6). An equilibrium model is now presented which has as its basis restricted internal rotation (7-10). This naturally leads to a physical picture wherein at low temperatures ($T < T_g$, where T_g is the glass temperature in °K.) the molecular segments are localized in potential energy wells, and undergo torsional vibrations. On the other hand, at extremely high temperatures ($T > T_g$) the motion will tend to approach free rotation about single bonds in the polymer chain.

It is seen that the region of interest lies intermediate to these two extremes, i.e., when $T \cong T_g$. The subsequent discussion is based upon a procedure developed and utilized by Pitzer and Gwinn (8).

The potential energy is considered to be a function of the angle of rotation about a given bond (if independence is assumed, then the total potential energy per polymer molecule is obtained by summation over the entire chain). In addition, the potential energy hindering rotation is assumed to be separable into an internal and an external part. For simplicity each component is considered to be a sinusoidal function with all of its minima (as well as maxima) of the same energy. Thus the total potential energy would have the following general form:

$$V = 1/2V_1(1 - \cos(n\phi)) + 1/2V_e(1 - \cos(m\phi + \alpha)) + \text{Const.} \qquad (1)$$

where V_i and V_e are the respective intramolecular and intermolecular barrier heights, n and m are the corresponding potential energy periodicities (symmetry numbers), ϕ is the angle of rotation out of the chosen plane of reference, and α is a possible phase difference in the angular distribution of the minima.

A particularly simple case arises when $m = n = 3$ and $\alpha = 0$; this will be used henceforth. Substitution in eq. (1) gives

$$V = 1/2(V_i + V_e)(1 - \cos 3\phi) = 1/2V_m(1 - \cos 3\phi) \qquad (2)$$

The classical partition function for rotation about the jth bond is

$$q_{j\ class} = (2\pi I_j kT/h^2)^{1/2} \int_0^{2\pi/3} \exp[-1/2V_m(1 - \cos 3\phi)/kT]d\phi \qquad (3)$$

where I_j is the reduced moment of inertia, h is Planck's constant, and k is the Boltzmann constant. A better approximation is obtained if one transforms $q_{j\ class}$ to q_j in the following manner (8,9):

$$q_j = q_{j\,class} \cdot q_{HO-Q}/q_{HO-C} \qquad (4)$$

where q_{HO-Q} and q_{HO-C} are the respective quantum and classical harmonic oscillator partition functions. The partition function for the entire molecule is given by the product over j.

If one were to plot the heat capacity derived from this partition function against temperature, a maximum would be observed. (In general this would occur at $V_m \cong 5kT_{max}$) (10,11). It is now proposed to identify T_{max} with T_g, which leads to the result that the glass temperature is proportional to the total barrier height energy.

It may be seen, therefore, that a lowering of V_e, e.g., by lowering the molecular weight of the polymer species, or by plasticization, would result in a lowering of T_g (the magnitude of lowering would depend upon the relative values of V_i and V_e).

It is noted that the relatively sharp rise in the heat capacity might be experimentally observed as a discontinuity. Also, a difference in the dynamic volume as rotation is increased could account for the change in dv/dT at T_g.

Finally, it is observed that the stiffening of the polymer chains (in the present sense) could lead to a rigid noncrystalline solid-like state, i.e., a glass.

It is acknowledged that part of this work was conceived at Brown University while the author was on a postdoctorate fellowship with Prof. J. H. Gibbs. Thanks is given to Dr. T. K. Kwei of the Interchemical Central Research Laboratories for many stimulating conversations relating to the present subject.

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γ-RAY INITIATED COPOLYMERIZATION OF ETHYLENE AND CARBON MONOXIDE*

The purpose of this note is to report the monomer reactivity for the copolymerization of ethylene and carbon monoxide initiated by Co^{60} γ-rays. The data of Brubaker et al. (1), and Coffman et al. (2), who synthesized this copolymer by conventional peroxide initiators were correlated and a comparison for (a) the ratio of specific rate constants was made.

Experimental

A number of runs were made in which the initial mole concentration of the two monomers was varied as shown in Table I.

TABLE I

Ethylene-Carbon Monoxide System[a]

Run No.	Initial monomer[b] mole ratio, A/B	Final polymer[c] mole ratio, a/b
32–15	3.00	1.16
32–8	3.44	1.21
32–12	4.29	1.16
32–10	5.29	1.28
32–17	9.78	1.41
32–7	11.93	1.46

[a] Dose rate = 156,000 rads./hr.; Total dose = 780,000 rads.; Initial pressure = 650 atm.; and Irradiation temperature = 20°C.

[b] A/B = initial E/CO mole ratio.

[c] a/b = final E/CO mole ratio.

The experiments were performed in static unstirred stainless steel vessels, at initial pressures of 680 atm. and room temperature. All irradiations were conducted in the Gamma Pool Facility at Brookhaven National Laboratory. The composition of the copolymer was determined by elementary analysis. The powdered samples were hot pressed into films with a Carver Press for infrared identification on a Perkin-Elmer Infracord 137 spectrophotometer.

*Work performed under the auspices of the U. S. Atomic Energy Commission, Division of Isotope Development.

Discussion and Results

The experimental data obtained in the study of the gamma initiated copolymerization of ethylene and carbon monoxide is given in Table I. Polymerizations were carried out to low conversions in order to minimize the possibility of depleting either of the monomers. The data in Table I were found to obey a simplified form of the copolymer composition equation (3-5):

$$\frac{b}{a} = \frac{B}{A} \cdot \alpha \cdot \frac{\beta B + A}{\alpha B + A} \qquad (1)$$

The above equation states that a mixture of the two monomers in the molar ratio B/A should yield an initial copolymer with the molar ratio b/a.

The assumption is made that if monomers A and B undergo reaction, free radicals of the type A· and B· are formed and react in four possible modes of monomer addition. The four reactions are governed by the propagation rate constants K_{aa}, K_{ab}, K_{ba}, and K_{bb}. The composition of the copolymer can be determined from the ratio of the rate constants:

$$\alpha = K_{ab}/K_{aa}, \qquad \text{and} \qquad \beta = K_{bb}/K_{ba}$$

If carbon monoxide is designated as component B of the monomer mixture, the rate constant K_{bb} vanishes and $\beta = 0$ since carbon monoxide

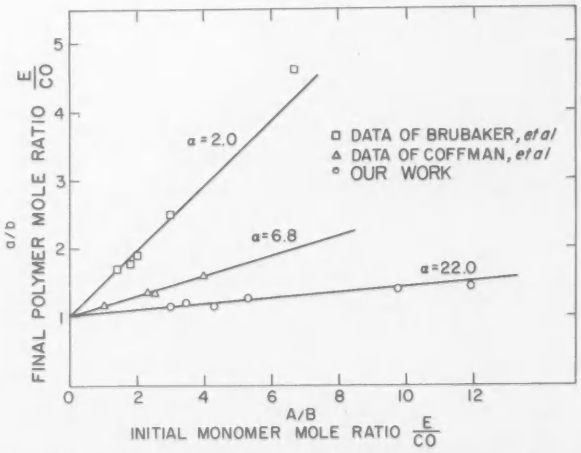

Fig. 1. A comparison of α values for ethylene-carbon monoxide copolymer systems.

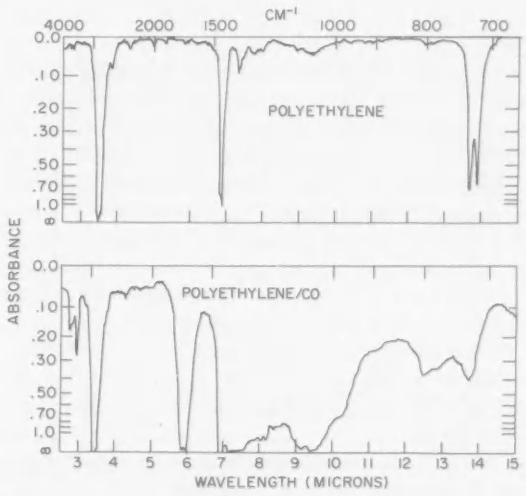

Fig. 2. Comparative I.R. spectra for polyethylene and polyethylene-carbon monoxide copolymer.

does not polymerize alone. In this case, eq. (1) reduces to the simplified form:

$$a/b = 1 + (A/\alpha B) \tag{2}$$

A plot of a/b vs. A/B, using the experimental data in Table I, yields a straight line of slope $1/\alpha$ with an intercept of 1, as predicted by eq. (2).

The data in Table I, as plotted in Figure 1, yields a straight line of the slope 1/22.0 (α = 22), indicating that carbon monoxide monomer adds 22 times as fast as an ethylene monomer to an ethylene free radical chain end.

In a similar manner, values for α were also calculated from experimental data presented by Brubaker et al. (1), and Coffman et al. (2), who studied the ethylene-carbon monoxide copolymer system using conventional peroxide initiators. The α value, calculated from Brubaker's data for experiments carried out in cyclohexane at 136 atm. and 135°C., was 2.0, while that for Coffman's data performed without solvent at pressures ranging from 850-1,000 atm. and temperatures between 120-130°C., was 6.8. The differences in experimental conditions may account for the wide variation of α values; however, it seems significant that in the radiation process the carbon monoxide is induced to add to an ethylene free radical chain end to a much greater degree than in the conventional free radical initiation process.

Figure 2 shows an infrared spectrum for the ethylene-carbon monoxide copolymer and for pure polyethylene produced by gamma radiation as described by Steinberg et al. (6).

The only characteristic polyethylene band remaining unaffected in the ethylene-carbon monoxide copolymer spectrum is the C–H stretch band at 3.4 μ. The change in the C–H bending vibration at 6.8 μ has been assigned to a methylene structure adjacent to a carbonyl. The doublet at 13.7 and 13.9 μ indicating four or more carbons in a chain became a singlet and decreased in intensity. The strong carbonyl absorption at 5.8 μ and its harmonic at 2.9 μ indicate a polyketone structure.

More detailed data on the experimental techniques and the physical and chemical properties of these copolymers will be published later.

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DETERMINATION OF GEL IN POLYMERS

Recognition of the importance of gel content of polymers and, hence, of a reliable technique for its determination, led to development of the technique described below. Even though a number of techniques exist for such a determination, it has been the experience of the authors that reasonable agreement is seldom obtained between gel concentrations determined by different laboratories on the same sample (even when the same technique is supposedly used).

The determination of gel in polymer is simple in theory. The requirements are: (a) All of the soluble polymer must be dissolved; (b) separation of the gel polymer from the polymer solution must be achieved; (c) the weight percentage of the gel (or of soluble polymer) must be accurately determined.

The difficulty with most of the methods presently in use is that requirements (a) and (b) are seldom accomplished together. In order to completely dissolve the soluble polymer in a reasonable amount of time, some degree of agitation is usually necessary. Such agitation often disperses some of the gel into fine particles whose isolation on a wire mesh screen is impossible. If the alternate technique of determining the concentration of the polymer solution is used, a certain quantity of this fine gel is counted as soluble polymer. If no agitation is used in the dissolving step, long periods of time are required for complete solution of soluble polymer. When the gel is finally obtained, it must be very thoroughly washed or soluble polymer trapped within will be counted as gel.

The present method was developed to satisfactorily cope with the above situations. In a typical gel determination, a 0.5 g. sample of polymer (cut into small pieces) and 100 ml. of a suitable solvent were placed in a 4 oz. glass bottle having a screw cap with an aluminum foil gasket. The tightly capped bottle was placed on a Burrell Wrist-Action Shaker (three hours sufficient in most cases) to dissolve the soluble polymer. The bottle was then removed from the shaker and centrifuged at 2500 rpm in an International Model SBV Centrifuge. After about 1 hr. of centrifugation, the clutch of the centrifuge was disengaged to allow the sample to come to a smooth stop. The bottle was carefully removed from the centrifuge, and a 25 ml. aliquot portion of the solution was removed from the upper half of the 100 ml. volume in the bottle to avoid picking up any particles of gel on the bottom. The aliquot was placed in a tared aluminum pan and dried gently with no spattering or excessive heat to constant weight. The conditions of centrifugation employed are believed sufficient to separate so-called microgel (gel particles of colloidal size which may impart a slight haze or turbidity to normally clear

TABLE I

Results of Gel Determinations for Various Polymers

Sample[a]	Per cent[b] soluble	Average error	Average per cent error	Per cent gel	Average error	Average per cent error
(BD/AN)–1	36.3			63.7		
	36.5	±0.20	±0.55	63.5	±0.20	± 0.32
	36.7			63.3		
(BD/AN)–2	64.7			35.3		
	62.8	±0.78	±1.22	37.2	±0.78	± 2.16
	64.5			35.5		
(BD/AN)–3	89.1	±0.50	±0.56	10.9	±0.50	± 4.80
	90.1			9.9		
SBR–1	91.6	±0.55	±0.60	8.4	±0.55	± 7.01
	92.7			7.3		
SBR–2	97.3			2.7		
	96.2	±0.38	±0.39	3.8	±0.38	±11.78
	96.8			3.2		
SBR–3	96.8			3.2		
	96.9	±0.07	±0.07	3.1	±0.07	± 2.26
	97.0			3.0		
BD–1	95.3			4.7		
	94.6	±0.47	±0.49	5.4	±0.47	± 9.92
	95.9			4.1		
BD–2	98.7			1.3		
	98.2	±0.30	±0.30	1.8	±0.30	±22.55
	99.1			0.9		
I	75.3	±0.25	±0.33	24.7	±0.25	± 1.00
	74.8			25.2		

[a] BD/AN is the copolymer of butadiene and acrylonitrile, SBR is the copolymer of butadiene and styrene, BD is the polybutadiene, and I is the polyisoprene.

[b] Benzene was the solvent used in all cases except for (BD/AN)–2 and –3, which used methyl ethyl ketone.

polymer solutions) and yet not extreme enough to settle large polymer molecules. The following equation was used to calculate percent gel:

$$\text{Per cent gel} = \frac{W_1 - (W_2 \times 4)}{W_1} \times 100$$

where W_1 and W_2 are the weights of initial sample and of dried residue, respectively.

This technique, although achieving complete solution of polymer and complete separation of gel from solution, is still subject to experimental error. The most important possible source of error is temperature variation. Since the volume of a solvent may change significantly with temperature, it is of great importance that the temperatures of solvent and solution be the same at the time of the original and final (aliquot) volume measurements.

This method was used to determine the per cent gel for a number of samples, and the results are shown in Table I. The samples were selected to provide several types of polymer and gel levels for the investigation. The data are presented both as per cent soluble polymer and as per cent gel to illustrate a rather obvious but important point. The excellent precision shown between determinations of per cent soluble polymer attests to the reliability of the experimental technique employed. However, although the average errors for the per cent gel values seem acceptable, the corresponding percentage errors are quite high in most cases. The highest percentage errors are observed for samples having low gel content. This is the case because the average error, defined as

$$a = \pm\frac{\Sigma d}{n}$$

where d is the deviation from the mean (m) and n is the number of observations, is the same for corresponding per cent soluble polymer and per cent gel data; while the average per cent error, $(a/m) \times 100$, is dependent on the value of the mean. The result is that the precision in the determination of per cent soluble polymer must be excellent in order to obtain good precision among per cent gel values. For this reason, and also since gel values are frequently not corrected for insoluble components other than crosslinked polymer, it might be better to report this type of data in terms of per cent soluble polymer.

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POLYBUTENE-1 – TYPE II CRYSTALLINE FORM

The unit cell of the Type II crystalline form of polybutene-1 has been described by Natta (1) as tetragonal with a = 7.49 A., c = 6.85 A. (fiber repeat), with one chain per cell in a 4_1 helical configuration; on drawing specimens of the unoriented crystalline polymer in the unstable Type II form it converts directly to the stable Type I modification.

We have obtained x-ray photographs of crystalline polybutene-1 fibers showing the Type II form well oriented, together with only a small amount of oriented Type I. The fibers were obtained from a narrow strip of polymer cut from a pressed sheet. This was held clamped at both ends and heated to 140°C., above the melting point of the Type I form, cooled to 90°C. to develop the Type II form, and then slowly drawn at 90°C. to the limit attainable without breakage. The fiber was then allowed to regain room temperature and photographed immediately before substantial conversion took place.

Weak layer lines were present between those characterising a repeat of 6.85 A. which showed that the fiber repeat was in fact 20.6 A., three times Natta's value. All reflections fit the basic tetragonal equatorial cell network proposed by Natta when the a dimension is doubled (a = 14.85 A.). The chain configuration is a helix with three turns in eleven monomer units. This gives a crystalline density for the Type II form of 0.90 g./cc. compared with 0.97 g./cc. for the unit cell and 4_1 helix proposed by Natta. The crystalline density of 0.90 g./cc. is consistent with our observed density of $\sim$0.87 g./cc. for specimens in the Type II form which are 40-45% crystalline and the density of amorphous polybutene-1, 0.85 g./cc. (2). Thus, as would be expected, the conversion from Type II to Type I (d = 0.95 g./cc. (2)) takes place from a form of lower density to one of higher density. For an 11_3 helix, the distance measured parallel to the chain axis per monomer unit is 1.87 A. compared with 2.17 A. per monomer unit for the Type I ternary helix which has a fiber repeat of 6.5 A. (2). The 11_3 helix is therefore less extended than the Type I helix and this difference will assist the conversion of Type II to Type I in samples subjected to the tension required to produce orientation.

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